[received by the International Bureau on 20 June 2005 (20.06.2005); original claims 1-95 are replaced by amended claims 1-50 (10 pages)]

What is claimed is:

1. A compound having the general structure:

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$$\begin{array}{ll} (R^2-SO_2-(Y^2)_q)_n \\ A^{1-}(R^1-SO_2-Y^1)_m \\ (R^3-SO_2-Y^3)_p \end{array} \qquad (I),$$

wherein A<sup>1</sup> is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings

 $R^1$ ,  $R^2$ , and  $R^3$  are divalent fluorinated groups; m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups; q is 0 or 1:

Y<sup>1</sup> is –OH, –NH-SO<sub>2</sub>-R<sup>4</sup> wherein R<sup>4</sup> is a monovalent fluorinated group, –NH–, –NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH–, or –NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH–, wherein A<sup>2</sup> is a divalent heterocyclic group and R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are divalent fluorinated groups; and Y<sup>2</sup> and Y<sup>3</sup> are –OH or –NH-SO<sub>2</sub>-R<sup>4</sup>; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y<sup>1</sup> is selected from the group consisting of –NH–, –NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH–, and –NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH–.

- 2. The compound of claim 1 wherein the compound is a small molecule.
- 3. The compound of claim 1 wherein the compound is a repeat unit for a polymer.
- 4. The compound of claim 1, 2 or 3 wherein A¹ selected from the group consisting of oxadiazole, triazole, thiadiazole, pyrazole, triazine, tetrazole, oxazole, thiazole, imidazole, benzoxazole, benzothiazole, benzobisoxazole, benzobisimidazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.
- 5. The compound of claim 4 wherein A<sup>1</sup> is selected from the group consisting of [1,3,4]oxadiazole, [1,3,4]thiadiazole, and [1,2,4]triazole,
- 6. The compound of claim 5 wherein A<sup>1</sup> is [1,3,4]oxadiazole.

7. The compound of claim 1, 2, or 3 wherein R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.

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- 8. The compound of claim 7 wherein R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are linear or branched perfluorinated saturated or unsaturated groups having 1 to 10 carbon atoms optionally containing ethereal oxygen atoms.
- 9. The compound of claim 8 wherein  $R^1$ ,  $R^2$ , and  $R^3$  are linear perfluorinated saturated groups having 1 to 6 carbon atoms.
- 10. The compound of claim 1, 2, or 3 wherein m + n + p is equal to 2 or 3.
  - 11. The compound of claim 10 wherein m + n + p is equal to 2.
  - 12. The compound of claim 1 or 3 wherein A<sup>2</sup> is a divalent aromatic heterocyclic group, such as an oxadiazole, triazole, thiadiazole, benzobisoxazole, benzobisthiazole, benzobisimidazole, bibenzoxazole, bibenzothiazole, and bibenzimidazole.
  - 13. The compound of claim 12 wherein A<sup>2</sup> is [1,3,4]oxadiazole.
- 20 14. The compound of claim 1 or 3 wherein R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated groups having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.
  - 15. The compound of claim 1 or 2 wherein  $Y^1$ ,  $Y^2$ , and  $Y^3$  are each equal to -OH or  $-NH-SO_2-R^4$ , wherein  $R^4$  is any monovalent fluorinated group, and q is 1.
  - 16. The compound of claim 15 wherein R<sup>4</sup> is a linear, branched, or cyclic perfluorinated or partially fluorinated saturated or unsaturated group having 1 to 20 carbon atoms optionally containing ethereal oxygen, chlorine, bromine, or iodine atoms.
    - 17. The compound of claim 15 wherein m + n + p is equal to 2 or 3.
  - 18. The compound of claim 1 or 2 wherein  $Y^1$  is -NH-SO<sub>2</sub>-R<sup>4</sup>, n and p are each equal to 0, and m is 2 or 3.
- 19. The compound of claim 1 or 3 wherein m and n is each equal to 1, p is 0 to 1, and q is 0.

20. The compound of claim 19 wherein  $A^1$  is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and  $Y^1$  is -NH—.

- 21. The compound of claim 19 wherein  $A^1$  is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and  $Y^1$  is -NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH-, wherein R<sup>5</sup> is a divalent fluorinated group.
- 22. The compound of claim 19 wherein  $A^1$  is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and  $Y^1$  is  $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$ , wherein  $R^6$  and  $R^7$  are a divalent fluorinated groups.
- 23. A compound of claim 1 or 3 wherein the compound is a random copolymer obtained by randomly combining any variety of the polymer repeat units, in any ratio with respect to each other, wherein m and n are each equal to 1, p is 0 to 1 and q is 0.
- 24. A compound of claim 1 or 2 wherein A<sup>1</sup> is a divalent aromatic heterocyclic group, m is 2, n and p are each equal to 0, and Y<sup>1</sup> is -NH-SO<sub>2</sub>-R<sup>4</sup>.
  - 25. A compound of claim 1 or 3 wherein  $A^1$  is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and  $Y^1$  is -NH-.
  - 26. A compound of claim 1 or 3 wherein  $A^1$  is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and  $Y^1$  is -NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH-.
- 27. A compound of claim 1 or 3 wherein A<sup>1</sup> is a divalent aromatic heterocyclic group, m and n are each equal to 1, p is 0, q is 0, and Y<sup>1</sup> is –NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH–.
  - 28. A fluorinated fluorosulfonyl-substituted heterocycle having the general structure:

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$$(R^{2}-SO_{2}-F)_{n}$$
  
 $A^{3}-(R^{1}-SO_{2}-F)_{m}$   
 $(R^{3}-SO_{2}-F)_{p}$  (II),

wherein  ${\sf A}^3$  is a divalent or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are divalent fluorinated groups;

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- m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 2 or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by fluorinated fluorosulfonyl groups.
- 29. The fluorinated fluorosulfonyl-substituted heterocycle of claim
   28 wherein A<sup>3</sup> is a divalent aromatic heterocyclic group, m and n are each equal to 1, and p is 0.
  - 30. The fluorinated fluorosulfonyl-substituted heterocycle of claim 28 wherein  $A^3$  is a divalent aromatic heterocyclic group, n and p are each equal to 0, and m is 2.
  - 31. A process for synthesizing a compound comprising the following steps:
  - (a) providing a fluorosulfonyl-containing acyl derivative having the structure:

## F-SO<sub>2</sub>-R<sup>8</sup>-X,

- wherein R<sup>8</sup> is a divalent fluorinated group as defined above for R<sup>1</sup> and X is an acyl group;
  - (b) condensing the fluorosulfonyl-containing acyl derivative from step (a) with a nitrogenous reagent to form a sulfonyl-containing precursor;
  - (c) cyclizing the sulfonyl-containing precursor of step (b) by thermolysis or dehydration to form a sulfonyl-containing aromatic heterocyclic compound containing fluorosulfonyl groups or sulfonamide groups; and
- (d) converting the sulfonyl-containing aromatic heterocyclic compound of step (c) containing fluorosulfonyl groups or sulfonamide
   groups, into an acidic sulfonyl-containing aromatic heterocyclic compound by either:
  - (i) condensing fluorosulfonyl groups with a fluorinated sulfonamide,
  - (ii) condensing sulfonamide groups with a fluorinated sulfonyl fluoride,
- (iii) condensing fluorosulfonyl groups first with ammonia to form sulfonamide groups followed by a fluorinated sulfonyl fluoride to

form sulfonimide groups, or

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- (iv) hydrolysis of fluorosulfonyl or sulfonamide groups to form sulfonic acid groups.
- 32. The process of claim 31 wherein the acyl group is selected from the group consisting of acyl fluoride, acyl chloride, acyl bromide, acyl lodide, an ester, an amide, and nitrile.
  - 33. The process of claim 31 wherein the nitrogenous reagent, is selected from the group consisting of ammonia; hydrazine; an azide; and an organic ortho-substituted aromatic amine.
- 34. A process for synthesizing a bis(sulfonimide)-[1,3,4]oxadiazole by condensing a fluorosulfonyl acyl fluoride, F-SO<sub>2</sub>-R<sup>8</sup>-GO-F, with hydrazine to form a bis(fluorosulfonyl)dihydrazide containing a dihydrazide group and fluorosulfonyl groups; forming a [1,3,4]oxadiazole ring by cyclizing the dihydrazide group using dehydration; condensing the fluorosulfonyl groups with ammonia to form a bis(sulfonamide)-[1,3,4]oxadiazole containing sulfonamide groups; and forming sulfonimide groups by condensing a fluorinated sulfonyl fluoride, R<sup>4</sup>-SO<sub>2</sub>-F, with the sulfonamide groups, wherein R<sup>4</sup> and R<sup>8</sup> are linear perfluorinated saturated groups having 1 to 6 carbon atoms.
- 35. A process for synthesizing a copolymer containing sulfonimide and [1,3,4]oxadiazole groups by condensing a fluorosulfonyl acyl fluoride, F-SO<sub>2</sub>-R<sup>8</sup>-CO-F, with hydrazine to form a bis(fluorosulfonyl)dihydrazide containing a dihydrazide group and fluorosulfonyl groups; forming a [1,3,4]oxadiazole ring by cyclizing the dihydrazide group using dehydration; condensing the fluorosulfonyl groups with ammonia to form a bis(sulfonamide)-[1,3,4]oxadiazole containing sulfonamide groups; and forming sulfonimide groups by condensing a fluorinated disulfonyl difluoride, F-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-F, with the sulfonamide groups, wherein R<sup>5</sup> and R<sup>8</sup> are linear perfluorinated saturated groups having 1 to 6 carbon atoms.
- 36. A process for synthesizing a benzimidazole sulfonimide by condensing a fluorosulfonyl acyl fluoride, F-SO<sub>2</sub>-R<sup>8</sup>-CO-F, with ammonia to form a diamide containing a carbamide group and a sulfonamide group; condensing the carbamide group with an ortho-phenylene diamine to form a carbamide adduct; cyclizing the carbamide adduct by thermolysis to form a benzimidazole group, and forming a sulfonimide group by condensing a fluorinated sulfonyl fluoride, R<sup>4</sup>-SO<sub>2</sub>-F, with the sulfonamide group,

wherein  $\ensuremath{\mathsf{R}}^4$  and  $\ensuremath{\mathsf{R}}^8$  are linear perfluorinated saturated groups having 1 to 6 carbon atoms.

- 37. A process for synthesizing a benzimidazole sulfonic acid by condensing a fluorosulfonyl acyl fluoride, F-SO<sub>2</sub>-R<sup>8</sup>-CO-F, with an orthophenylene diamine to form a carbamide adduct; cyclizing the carbamide adduct by thermolysis to form a benzimidazole group, and forming a sulfonic acid group by hydrolyzing the fluorosulfonyl group wherein R<sup>8</sup> is a linear perfluorinated saturated group having 1 to 6 carbon atoms.
- 38. A solid polymer electrolyte membrane comprising a porous substrate having imbibed therein a compound having the general structure:

$$\begin{array}{ccc} (R^2 - SO_2 - (Y^2)_q)_n \\ A^1 - (R^1 - SO_2 - Y^1)_m \\ (R^3 - SO_2 - Y^3)_p \end{array} \qquad (I),$$

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wherein A<sup>1</sup> is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are divalent fluorinated groups;

- 20 m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups; q is 0 or 1;
- Y<sup>1</sup> is –OH, –NH-SO<sub>2</sub>-R<sup>4</sup> wherein R<sup>4</sup> is a monovalent fluorinated group, –NH–, –NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH–, or –NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH–, wherein A<sup>2</sup> is a divalent aromatic heterocyclic group and R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are divalent fluorinated

groups; and Y<sup>2</sup> and Y<sup>3</sup> are –OH or –NH-SO<sub>2</sub>-R<sup>4</sup>; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y<sup>1</sup> is selected from the group consisting of –NH–, –NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH–, and –NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH–.

39. The solid polymer electrolyte membrane of claim 38 wherein the porous substrate is selected from the group consisting of inorganic fiber substrates and microporous films of perfluorinated polymers.

- 40. The solid polymer electrolyte membrane of claim 38 wherein the compound is a small molecule.
- 41. The solid polymer electrolyte membrane of claim 38 wherein the compound is a repeat unit for a polymer.
- 42. The solid polymer electrolyte membrane of claim 38 wherein the compound is cross linked, grafted, or chain extended within the porous support.
- 43. The solid polymer electrolyte membrane of claim 42 wherein the compound is modified to contain reactive functional groups to provide crosslinking, grafting, or chain extension.
- 44. The solid polymer electrolyte membrane of claim 42 wherein
   the compound is mixed with reagents to provide crosslinking, grafting, or chain extension.
  - 45. A catalyst coated membrane comprising a solid polymer electrolyte membrane having a first surface and a second surface, an anode present on the first surface of the solid polymer electrolyte membrane, and a cathode present on the second surface of the solid polymer electrolyte membrane, wherein the solid polymer electrolyte membrane comprises a porous substrate having imbibed therein a compound having the general structure:

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wherein A<sup>1</sup> is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups; q is 0 or 1;

- Y<sup>1</sup> is -OH, -NH-SO<sub>2</sub>-R<sup>4</sup> wherein R<sup>4</sup> is a monovalent fluorinated group, -NH-, -NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH-, or -NH-SO<sub>2</sub>-R<sup>8</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH-, wherein A<sup>2</sup> is a divalent aromatic heterocyclic group and R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are divalent fluorinated groups; and
- Y<sup>2</sup> and Y<sup>3</sup> are -OH or  $-NH-SO_2-R^4$ ; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y<sup>1</sup> is selected from the group consisting of -NH-,  $-NH-SO_2-R^5-SO_2-NH-$ , and  $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$ .
- 46. A membrane electrode assembly comprising a polymer electrolyte membrane having a first surface and a second surface, and comprising a compound having the general structure:

$$(R^{2}-SO_{2}-(Y^{2})_{q})_{n}$$
  
 $A^{1}-(R^{1}-SO_{2}-Y^{1})_{m}$   
 $(R^{3}-SO_{2}-Y^{3})_{p}$  (I),

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wherein  ${\sf A}^1$  is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are divalent fluorinated groups;

- 25 m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups; q is 0 or 1;
- Y<sup>1</sup> is -OH, -NH-SO<sub>2</sub>-R<sup>4</sup> wherein R<sup>4</sup> is a monovalent fluorinated group, -NH-, -NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH-, or -NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH-, wherein A<sup>2</sup> is a divalent aromatic heterocyclic group and R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are divalent fluorinated groups; and

 $Y^2$  and  $Y^3$  are -OH or -NH-SO<sub>2</sub>-R<sup>4</sup>; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0,  $Y^1$  is selected from the group consisting of -NH-, -NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH-, and -NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH-.

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47. An electrocatalyst coating composition comprising a compound having the general structure:

$$\begin{array}{l} (R^2 - SO_2 - (Y^2)_q)_n \\ \stackrel{\wedge}{h}^{1} - (R^1 - SO_2 - Y^1)_m \\ (R^3 - SO_2 - Y^3)_p \end{array} \tag{I),}$$

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wherein A<sup>1</sup> is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are divalent fluorinated groups; m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1, 2, or 3 so that the carbon atoms of the heterocyclic rings are fully substituted by acidic fluorinated sulfonyl-containing groups; q is 0 or 1;

Y<sup>1</sup> is –OH, –NH-SO<sub>2</sub>-R<sup>4</sup> wherein R<sup>4</sup> is a monovalent fluorinated group, –NH–, –NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH–, or –NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH–, wherein A<sup>2</sup> is a divalent aromatic heterocyclic group and R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are divalent fluorinated groups; and

Y<sup>2</sup> and Y<sup>3</sup> are -OH or -NH-SO<sub>2</sub>-R<sup>4</sup>; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y<sup>1</sup> is selected from the group consisting of -NH-, -NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH-, and -NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH-.

48. An electrocatalyst coating composition of claim 47 further comprising a catalyst.

49. An electrochemical cell comprising a polymer electrolyte membrane, wherein the polymer electrolyte membrane comprises a compound having the general structure:

$$\begin{array}{l} (R^2 - SO_2 - (Y^2)_q)_n \\ \mathring{h}^{1-} (R^1 - SO_2 - Y^1)_m \\ (R^3 - SO_2 - Y^3)_p \end{array} \qquad (i),$$

wherein A<sup>1</sup> is a monovalent, divalent, or trivalent aromatic heterocyclic group comprising heterocyclic rings;

R<sup>1</sup>, R<sup>2</sup>, and R<sup>3</sup> are divalent fluorinated groups;

m, n, and p are 0 to 3, with the proviso that m + n + p is equal to 1,

2, or 3 so that the carbon atoms of the heterocyclic rings are fully

substituted by acidic fluorinated sulfonyl-containing groups; q is 0 or 1;

Y<sup>1</sup> is -OH, -NH-SO<sub>2</sub>-R<sup>4</sup> wherein R<sup>4</sup> is a monovalent fluorinated group, -NH-, -NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH-, or

-NH-SO<sub>2</sub>-R<sup>6</sup>-A<sup>2</sup>-R<sup>7</sup>-SO<sub>2</sub>-NH-, wherein A<sup>2</sup> is a divalent aromatic

heterocyclic group and R<sup>5</sup>, R<sup>6</sup>, and R<sup>7</sup> are divalent fluorinated groups; and

Y<sup>2</sup> and Y<sup>3</sup> are -OH or -NH-SO<sub>2</sub>-R<sup>4</sup>; with the proviso that when m and n are each equal to 1, p is 0 to 1, and q is 0, Y<sup>1</sup> is selected from the group consisting of -NH-, -NH-SO<sub>2</sub>-R<sup>5</sup>-SO<sub>2</sub>-NH-, and

 $-NH-SO_2-R^6-A^2-R^7-SO_2-NH-$ 

50. The electrochemical cell of claim 49 selected from the group consisting of fuel cells, batteries, chloralkali cells, electrolysis cells, sensors, electrochemical capacitors, and modified electrodes.